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AUTHOR(S):

Wakai, Chihiro; Shimoaka, Takafumi; Hasegawa, Takeshi

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# $^1\text{H}$ NMR Analysis of Water Freezing in Nanospace Involved in a Nafion Membrane

*Chihiro Wakai, Takafumi Shimoaka and Takeshi Hasegawa\**

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

**ABSTRACT:** Water involved in a polyelectrolyte membrane of Nafion has recently been revealed to comprise three distinctive molecular species with respect to molecular motion correlated with the hydrogen (H) bonding structure by using  $^1\text{H}$  NMR, infrared and mass spectrometries. The three species are assigned to the condensed water, hydration water, and strongly bounded water on the sulfonic acid group. In the present study, on the contrary to an expectation on this schematic, even the condensed water is found unfrozen when the membrane is cooled down to  $-50\text{ }^\circ\text{C}$ , and a freezing begins when it is cooled down to  $-60\text{ }^\circ\text{C}$  or lower. Two third of the condensed water remains unfrozen even at  $-80\text{ }^\circ\text{C}$ , which is attributed to the effect of nanospace where the water molecules are too short to construct the ice-like structure. The reduction of rotational motion of water is, on the other hand, commonly found for all the water species revealed via the calculation of the activation energies.

**KEYWORDS:** Nafion, adsorbed water, NMR, rotational correlation time

## INTRODUCTION

Nafion<sup>®</sup> is a polymer electrolyte, and a Nafion membrane is widely used in a fuel cell due to a high electrical conductivity induced by the adsorbed water yielding a uniquely high proton transportation character across the membrane. Since Nafion roughly comprises the perfluoroalkyl backbone and the hydrophilic sulfonic acid groups, the water adsorption occurs mainly about the hydrophilic group. To understand the proton transportation, the hydration structure about the sulfonic acid group is crucial, and the interrelationship between the adsorbed water and the conductivity has long been studied extensively by means of infrared (IR),<sup>1-3</sup> NMR,<sup>4-7</sup> small-angle X-ray scattering (SAX),<sup>8</sup> and neutron diffraction<sup>9</sup> etc.

The recent standard schematic of the hydration structure is the cluster-network model,<sup>10-14</sup> in which two kinds of water species are pointed out by various experimental studies. Iwamoto et al.,<sup>1</sup> for example, discussed the water in Nafion using IR spectroscopy in a drying process and found that the water species are categorized into two species: the directly hydrated water on the sulfonic acid group and the condensed water surrounding the hydration water. Zhao et al.<sup>5</sup> measure diffusivity of water in the membrane, and states that the sulfonic acid group is surrounded by two hydration shells that correspond to the hydration and condensed water species. In this manner, the fundamental picture of the hydration structure is related to the two water species.

Recently, however, the third water species has been found by using <sup>1</sup>H NMR spectroscopy. The newly found third water has an extraordinary long rotation-correlation time (220 ns) obtained by measuring the spin-lattice relaxation time, which is much longer than that of the hydration water (8.8 ns) and the condensed water (0.009 ns). This straightforwardly implies that the motion of the third water is strongly restricted. To explore the reason of the

strong motion restriction, the same sample has also been subjected to an IR analysis followed by a precise analysis with an aid of quantum chemical calculation. As a result, a “thoroughly dried” membrane is found to possess a single water molecule involved in a ring-like structure of the sulfonic acid group via two hydrogen bondings.<sup>3</sup> The coordination with the two hydrogen bondings readily explains the strong restriction of water. In addition, this coordination is fairly strong, and the “strongly bound water” is not removed when the sample is heated over 200 °C, and the water comes out with the sulfonic acid group as a thermally decomposed complex when the temperature reaches 300 °C, which has readily been confirmed by evolved gas analysis -mass spectrometry (EGA-MS). In this manner, the essential figure of the third water has been revealed.

In the present study, on this new schematic picture having the three water species, the freezing process of water has been pursued by using <sup>1</sup>H NMR. Since both the strongly bound water and the hydration water are motion restricted, the rest “condensed” water is expected to be frozen by cooling, which should be monitored by a decrease of the NMR peak of water.

As a result, water freezing does not occur until the sample is cooled down to -60 °C, which agrees with another report made by conductivity measurements. The present analysis has further revealed that only a half of the condensed water is frozen even if the sample is cooled at -90 °C. On the other hand, the rotational motion evaluated by obtaining the activation energy is found to be reduced below -60 °C, which is commonly found for all the water species.

## MATERIALS AND METHODS

**Materials:** The sample membrane was a Sigma-Aldrich (St. Louis, MO, USA) Nafion NRE-212 membrane with a thickness of 50 μm. The membrane was cut into a ribbon piece with a size of 2 mm x 50 mm. The sample was washed by 3% hydrogen peroxide aqueous solution at 100 °C for 1 h followed by 1M sulfonic acid aqueous solution at 100 °C for 1 h to remove metallic cations

remaining about the sulfonic acid group, which was further rinsed by pure water. The washed membrane was dried in an oven at 40 °C for 12 h.

The water was obtained by a Millipore (Molsheim, France) Elix UV-3 pure-water generator and a Yamato (Tokyo, Japan) Autopure WT100U water purifier, which is a compatible model of Milli-Q. The water exhibited an electric resistivity higher than 18.2 MΩ cm, and the surface tension was 72.5 mN m<sup>-1</sup> at 25 °C, which was measured by using a Kyowa Interface Science Co., Ltd. (Saitama, Japan) DropMaster, DM-501Hy, contact-angle meter. The water vapor was adsorbed by the Nafion membrane at 30 °C for 72 h using the same homemade equipment in a NMR tube as described in our previous work.<sup>7</sup>

**NMR Measurements:** The one-dimensional <sup>1</sup>H NMR spectra were measured by using a JEOL (Tokyo, Japan) ECA600 NMR spectrometer (600 MHz). Pure heavy water was used as the external reference of the chemical shift, and the standard signal was set to 4.72 ppm at 30 °C. The temperature was changed from +30 to -90 °C. At each temperature, thirty min was spent before the measurement, so that the water adsorption would reach equilibrium. The FID signal was accumulated 16 times. Digital resolution was 0.344 Hz.

## RESULTS AND DISCUSSION

**Partial Freezing of Water in Nafion:** Figure 1 shows <sup>1</sup>H NMR spectra of a Nafion membrane involving water at various temperatures from +30 down to -90 °C. The bulky water yields a peak at 4.7 ppm as described in the experimental section, and it is shifted toward a lower magnetic field when electrons about the water are drawn by a neighboring chemical group.<sup>15,16</sup> Thus, the sharp and strong peak at 7.12 ppm (30 °C) is assigned to water near the sulfonic acid group in Nafion.<sup>7</sup> The very minor satellite peak at 3.4 ppm comes from water vapor remained in the NMR tube, which disappears at 0 °C. The shift of the main peak to a lower magnetic field

with decreasing temperature is due to the enhancement of intermolecular interactions via hydrogen bonds. In addition, this peak becomes broader with cooling, which reflects a decrease of the rotational motion of water molecules<sup>17</sup> as discussed in detail later.

In a previous paper,<sup>7</sup> three distinctive water species were revealed to coexist about the sulfonate group in Nafion by using <sup>1</sup>H NMR. The analytical results show that, if they were readily measured distinctively, they should yield three peaks at 9.52, 6.73, and 4.61 ppm, which are assigned to the strongly bound, the hydrated, and the condensed water species, respectively, at 30 °C. The variance of the chemical shifts,  $\Delta\delta$ , of the three species of 4.91 (= 9.52 – 4.61) ppm corresponds to 2946 Hz on the 600 MHz NMR spectrometer. If the proton exchanging time of the water species is longer than 0.34 ms (= 1/(2946 Hz)), the three components would readily be resolved to yield three distinctive peaks in the spectra. Unfortunately, the exchanging time is adequately shorter than the  $\mu$ s range, however, and an averaged single peak is thus always generated. Regardless, if one of the species is frozen to stop the molecular motion on cooling, the peak area would apparently be decreased. Therefore, quantitative analysis on the peak area is necessary in the present study.

In Figure 2, the peak top position is plotted against temperature. The chemical shift ( $\delta$ ) becomes larger with a decrease of temperature due to the development of the hydrogen bonds. The shift rate on temperature ( $\Delta\delta/\Delta T$ ) is a constant at -0.0033 ppm K<sup>-1</sup> in the temperature range between +30 and -40 °C, which is about one-third of that of normal liquid water.<sup>18</sup> The small rate implies that the adsorbed water involved in Nafion has a largely different characteristic from that of bulky water. When the temperature goes down across -50 °C, the slope changes apparently: the rate gets down to another constant value of -0.010 ppm K<sup>-1</sup> in the range between -60 and -90 °C, which implies that the chemical atmosphere about the adsorbed water species changes at

about -60 °C. Since the species of the condensed (bulky) water is expected to be frozen below 0 °C, it is interesting to find that the shift rate keeps constant in the wide range from +30 °C down to -50 °C.

To discuss the water quantity in more detail, the proton-density variation is evaluated by using the area of an NMR peak. The area intensity,  $I$ , is proportional to the proton density,  $N$ , and the population difference between the parallel and anti-parallel spins to the Zeeman field,  $p_+$  and  $p_-$ , respectively, as follows:

$$I \propto N(p_+ - p_-). \quad (1)$$

The population ratio of  $p_-/p_+$  is expressed by using the Boltzmann factor:

$$\frac{p_-}{p_+} = \exp\left(-\frac{\Delta E}{k_B T}\right). \quad (2)$$

Here,  $\Delta E$  is the energy difference of the parallel and anti-parallel spin states ( $\Delta E = E_- - E_+ > 0$ ), and it is related to the magnetic field strength,  $H$ , through the gyromagnetic ratio of proton,  $\gamma$ .

$$\Delta E = \gamma \hbar H \quad (3)$$

When the relationship of  $p_+ + p_- = 1$  is taken into account, the following equation is obtained.

$$p_+ - p_- = \frac{\exp\left(\frac{\Delta E}{k_B T}\right) - 1}{\exp\left(\frac{\Delta E}{k_B T}\right) + 1} \approx \frac{\Delta E}{2k_B T} = \frac{\gamma \hbar H}{2k_B T} \quad (4)$$

Since  $\Delta E$  is much smaller than the energy due to the atmospheric temperature,  $k_B T$ , with a factor of  $10^{-4}$ , the exponential factor is simplified by Taylor expansion to obtain the last term of Eq. (4). The NMR peak intensity is thus interrelated with temperature by considering Eq. (1) as:

$$I \propto N \frac{\gamma \hbar H}{2k_B T} \Leftrightarrow N \propto \frac{2k_B}{\gamma \hbar H} IT. \quad (5)$$

In this manner, the product of peak intensity and temperature,  $IT$ , is found to be a good measure to discuss the proton density,  $N$ .

On this theory, the proton density is calculated as plotted by the open circles in Figure 3. In the initial cooling process from +30 to -20 °C, the proton density linearly increases slightly (solid line), which is attributed to the decrease of the volume due to the thermal contraction of the polymer matrix. Bauer et al. reports the temperature dependence of the length of a Nafion membrane.<sup>19</sup> At a relative humidity of 100%, the thermal contraction coefficient is about  $2.5 \times 10^{-3} \text{ K}^{-1}$  (read from Fig. 8 in Ref. 19), which is similar to our case ( $1.6 \times 10^{-3} \text{ K}^{-1}$ ).

At -40 °C, the open circle is off the line, which means that another factor is needed to understand the decrease than the thermal contraction, and partial freezing can be a good candidate. In fact, the decrease of the proton density is expanded to attain 10% at -60 °C. This extra-decrease should be attributed to the partial freezing of water in Nafion. To discuss the molar ratio of the frozen water, the number of each molecular species should be known.

**Counting Bound-Water Molecules:** In a previous report, the quantities of the strongly bound and the hydrated water species were analyzed on an assumption that the water adsorption begins from a **thoroughly dried state**. In a recent analysis, however, the chemical model has been corrected after a precise analysis using IR spectroscopy: a sulfonate group keeps a single water molecule making a ring-like complex even at a high temperature of 300 °C, which is confirmed by quantum chemical calculation and mass spectrometry. On this model, the quantity of water adsorption on the sulfonate group is reevaluated as follows.



At the initial state ( $t = 0$ ) in the wetting process, the protons observed by  $^1\text{H}$  NMR are provided by the sulfonate group and the single water molecule. Here, the number ratio of the water molecule to the sulfonic acid group is unity ( $[\text{SO}_3\text{H}] = [\text{H}_2\text{O}]$ ). Therefore, the proton concentration at  $t = 0$ ,  $[\text{H}]_0$ , is written as:

$$[\text{H}]_0 = [\text{SO}_3\text{H}] + 2 [\text{H}_2\text{O}] = 3 [\text{SO}_3\text{H}]. \quad (6)$$

The next hydration on this sulfonate-water complex is represented by the linear part 1 in Figure S1, which ends at the kink of  $[\text{H}]_0/[\text{H}]_t = 0.43$ . Here,  $[\text{H}]_t$  is the proton concentration at any time,  $t = t$ . At this proton concentration,  $[\text{H}]_t$  is expressed by considering Eq. (6) as:

$$\frac{[\text{H}]_t}{[\text{H}]_0} = \frac{[\text{H}]_t}{3[\text{SO}_3\text{H}]} = \frac{1}{0.43} \Leftrightarrow [\text{H}]_t = \left(\frac{3}{0.43}\right) \cdot [\text{SO}_3\text{H}]. \quad (7)$$

As a result, the “strongly bound (1st hydration) water” molecules involving the initial single water are counted as:

$$[\text{H}_2\text{O}]_{\text{1st-hydr}} = \frac{[\text{H}]_t - [\text{SO}_3\text{H}]}{2} = \left(\frac{\frac{3}{0.43} - 1}{2}\right) [\text{SO}_3\text{H}] = 3.0 [\text{SO}_3\text{H}]. \quad (8)$$

In this manner, the “strongly bound water” is found to comprise 3.0 water molecules about a sulfonic acid group. Thus analytical result agrees with a former report,<sup>3</sup> “three” water molecules are necessary to make a sulfonic acid group cationized to be a sulfonate group after stabilizing  $\text{H}^+$ . In other words, the sulfonic acid group keeps the electrically neutral form with less than three water molecules. In this manner, the first hydration process has been found to correspond to the hydration on a “neutral” sulfonic acid group.

The second hydration process is represented by the linear part of 2+2' in Figure S1 with the end point at  $[\text{H}]_0/[\text{H}]_t = 0.19$ . In a similar manner to the previous analysis, the summation of the first and second hydration water molecules are counted as:

$$[\text{H}_2\text{O}]_{1\text{st-hydr}} + [\text{H}_2\text{O}]_{2\text{nd-hydr}} = \frac{[\text{H}]_t - [\text{SO}_3\text{H}]}{2} = \left( \frac{\frac{3}{0.19} - 1}{2} \right) [\text{SO}_3\text{H}] = 7.4 [\text{SO}_3\text{H}]. \quad (9)$$

Since the first hydration water has already been revealed as  $[\text{H}_2\text{O}]_{1\text{st-hydr}} = 3.0 [\text{SO}_3\text{H}]$ , the second hydration water molecules are counted as 4.4. Note that, in this process, the core sulfonic acid has been changed to be a “sulfonate” group by releasing  $\text{H}^+$  that is stabilized by three or more water molecules.

In a similar manner, the third hydration process is calculated. The third water corresponds to the “condensed water.”<sup>7</sup> At 30 °C ( $t = 0$ ), the three water species yield a single NMR peak at 7.12 ppm (Figure 1). When this chemical shift is referred to the previous paper (or Figure S1), the proton concentration is found at  $[\text{H}]_0/[\text{H}]_t = 0.15$ . Therefore, the total number of hydrated water molecules is calculated as:

$$[\text{H}_2\text{O}]_{1\text{st-hydr}} + [\text{H}_2\text{O}]_{2\text{nd-hydr}} + [\text{H}_2\text{O}]_{3\text{rd-hydr}} = \left( \frac{\frac{3}{0.15} - 1}{2} \right) [\text{SO}_3\text{H}] = 9.5 [\text{SO}_3\text{H}] \quad (10)$$

In this manner, the third water molecules involved in the sample are counted as 2.1.

**Molar Ratio of Frozen Water Encapsulated in Nanospace:** Through the quantitative discussion in the previous section, the strongly bound, hydrated and condensed water species consist of 3.0, 4.4 and 2.1 water molecules at a polar (sulfonic acid or sulfonate group) group, respectively. In these water species, the condensed water should be ready for freezing; whereas the rest waters would be difficult to be frozen, since they are trapped via hydrogen bonding on the polar group. If the condensed water is totally frozen, the NMR peak would be decreased by 22% ( $= 2.1/9.5$ ).

As described above for Figure 3, the index of  $IT$  slightly increases because of the volume decrease (thermal contraction), which is presented by the solid line. As an approximation, the solid line is extrapolated linearly by the dotted line, from which the “freezing line” is predicted by considering 22%, which is drawn by the dashed line. If only the condensed water species are frozen, the value of  $IT$  is expected down to the freezing line.

If the “condensed water” is chemically the same as the normal bulky water, the water should begin to be frozen at about 0 °C, and the condensed water should totally be frozen at -60 °C. As a matter of fact, however, the decrease attains 7% even at -60 °C, which is about one-third of the predicted decrease (22%). This incomplete freezing strongly implies that the third hydration water comprises a molecular “cluster” that is far from the bulky water.

The data in the range from -60 to -80 °C<sup>20</sup> show a similar trend to those in the range from +30 to -20 °C (solid line in Fig. 3). This slight increase is thus also attributed to the thermal contraction. On the other hand, an apparent decrease is found at -90 °C suggesting a freezing of water. Regardless, for the very broad peak, an analytical error cannot be removed out even by using the curve-fitting technique.<sup>20</sup> At least we can say, however, that a partial freezing begins at -40 °C, which indicates that the “condensed water” in Nafion has a largely different structure from the normal condensed bulky water.

**Dynamics Analysis of Water:** To study the intrinsic difference between the newly found hard-to-freeze water and the normal condensed water, the dynamics of water is studied by using the half width at half height (HWHH) of the adsorbed water peak in the NMR spectra. HWHH is proportional to the inversed spin-spin relaxation time,  $1/T_2$ , as follows.

$$\text{HWHH} = \frac{1}{\pi T_2} \quad (11)$$

Although the direct measurements of  $T_2$  would be ideal, the minute water molecules in Nafion are too short to obtain a good quality spectrum, and therefore the indirect analysis via HWHH is employed in this study.

Before discussing  $T_2$  in terms of the rotational dynamics of “molecules,” a rough image of  $T_2$  as a function of the inversed temperature is plotted in Figure 4, which is an Arrhenius plot. Apparently two linear regions appear, and the slope changes at about  $-50\text{ }^{\circ}\text{C}$  ( $1/T = 4.5 \times 10^{-3}$ ), which is consistent with the previous discussion on Figures 2 and 3. On referring to reports by other research groups, the inflection point varies a lot. For example, MacMillan and co-workers also report<sup>4</sup> that the inflection temperature appears at  $-10\text{ }^{\circ}\text{C}$  that is apparently below  $0\text{ }^{\circ}\text{C}$ , but it is much higher than our result, although they employ a similar experimental condition with a water content of 15.9 w/w% to ours (14 w/w%). Boyle and co-workers, on the other hand, report that the inflection point appears at a very low temperature of  $-97\text{ }^{\circ}\text{C}$ .<sup>21</sup> Another inflection point is reported via measurements of the electric conductivity: Uosaki et al. report<sup>22</sup> that it appears at  $-63\text{ }^{\circ}\text{C}$ , which is quite close to our result. According to Siu et al.,<sup>23</sup> however, a similar analysis on the conductivity shows that the inflection occurs at a very high temperature of  $-6\text{ }^{\circ}\text{C}$ . In this manner, the analytical results would strongly depend on the sample condition, and the absolute values of different groups are difficult to be compared to each other. Of importance is that, however, the results on an identical sample are consistent as found in our present analysis.

The inflection point might be attributed to structural change of the Nafion membrane, which induces dynamics change of water. MacMillan et al., however, measured the relaxation time of  $^{19}\text{F}$  by NMR as a function of temperature, and no inflection point was found in a wide temperature range from  $+111$  to  $-87\text{ }^{\circ}\text{C}$ .<sup>4</sup> Therefore, the inflection point can simply be attributed to the dynamics change of “water.”

To evaluate the rotational activation energy of water, the rotational correlation time,  $\tau_c$ , is calculated by using the BPP theory<sup>17,24</sup> as represented by Eq. (12) in SI unit.

$$\frac{1}{T_2} = \frac{3}{20} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma^4}{r^6} \left( 3\tau_c + \frac{5\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right) \quad (12)$$

Here,  $\mu_0$  is the magnetic permeability in vacuum,  $\hbar$  is the Plank constant divided by  $2\pi$ ,  $\gamma$  is the gyromagnetic ratio of proton,  $r$  is the distance between two protons in a water molecule, and  $\omega_0$  is the angular frequency corresponding to the Larmor frequency. The inter-nuclear distance,  $r$ , was fixed to 0.151 nm by considering the typical value of gaseous water.<sup>7,25</sup> By solving the equation,  $\tau_c$  was obtained for each  $T_2$ .

The calculated  $\tau_c$  is plotted in Figure 5 against the inversed temperature to have another Arrhenius plot. The values at -60 °C or lower are significantly larger than those at -40 °C or higher. Since the rotational correlation time becomes larger when the molecular motion is restricted, this result straightforwardly indicates that the water molecules at -60 °C or lower are difficult to move. A quantitative evaluation of the molecular motion in the two temperature ranges is as follows.

The activation energy of the rotational motion is calculated from this Arrhenius plot. In the temperature range of +30 to -40 °C, the slope of the linear part yields the activation energy of 7.0 kJ mol<sup>-1</sup>. This energy is much smaller than that of normal liquid water (19 kJ mol<sup>-1</sup> at 30 °C<sup>26</sup>); whereas it is fairly close to that of water dispersed in a hydrophobic organic solvent such as carbon tetrachloride (8.6 kJ mol<sup>-1</sup>) and chloroform (9.3 kJ mol<sup>-1</sup>).<sup>26</sup> The water molecules involved in Nafion thus proved to lose a bulky character even for the “condensed” water, which should reflect the small number (2.1) of the condensed water molecules. On the other hand, at a temperature below -60 °C, the activation energy is obtained as 30.0 kJ mol<sup>-1</sup>. Although this is

four times larger than the higher temperature range, it is far smaller than the water in ice,  $55.6 \text{ kJ mol}^{-1}$ ,<sup>27</sup> which implies that the “frozen” water is not involved in a tight framework like the ice structure.

$^1\text{H}$  NMR observes the three water species as an averaged species because of the rapid proton exchange. When only the condensed water is frozen, therefore, the change of a physical parameter should be largely reduced. The four times increase of the activation energy, therefore, indicates that the motion of “all the species” is highly restricted under the low temperature, although a portion of the condensed water is frozen.

## CONCLUSION

To study the recently-found condensed water involved in the hydrated water molecules about the sulfonate group in Nafion, a series measurements of both chemical shift and **spin-spin relaxation time** were performed by using  $^1\text{H}$  NMR in a cooling course from  $+30$  through  $-90$  °C. By considering that the observed quantity of NMR is influenced by molecular motion, a new index that relates the quantity of water to the peak intensity is analytically deduced. With the new index, the water molecules are found not frozen even at  $-50$  °C, and begin to freeze  $-60$  °C or lower. At a very low temperature of  $-90$  °C, regardless, only a portion of the condensed water is frozen up to ca. two third. In our previous paper, the “condensed water” is revealed to have a common molecular dynamics to the normal bulk water at an ambient temperature in terms of chemical shift and the spin-lattice relaxation. The present result reveals, however, that the molecular “coordination structure” of the condensed water in nanospace is largely different from that of the bulk water. In nanospace, the small number of water molecules cannot construct the ice-like coordination. On the other hand, apart from the structure, the molecular “motion” is found to be commonly decreased for all the water molecules involved in Nafion below  $-60$  °C.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: htakeshi@scl.kyoto-u.ac.jp

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**Supporting Information Available:** Figure S1 is available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## FIGURE CAPTIONS

**Figure 1.**  $^1\text{H}$  NMR spectra of a hydrated Nafion membrane at various temperatures from +30, 0, -20, -40, -60, -80, and -90 °C.

**Figure 2.** Temperature dependence of the chemical shift,  $\delta$ , of the peak of water molecules adsorbed in Nafion.

**Figure 3.** Quantity change of a newly introduced measure,  $IT$ , against temperature.

**Figure 4.** Arrhenius plot of the spin-spin relaxation time,  $T_2$ , of water obtained by HWHH of the water peak.

**Figure 5.** Arrhenius plot of the rotational correlation time,  $\tau_c$ , of water calculated by using the BPP theory.

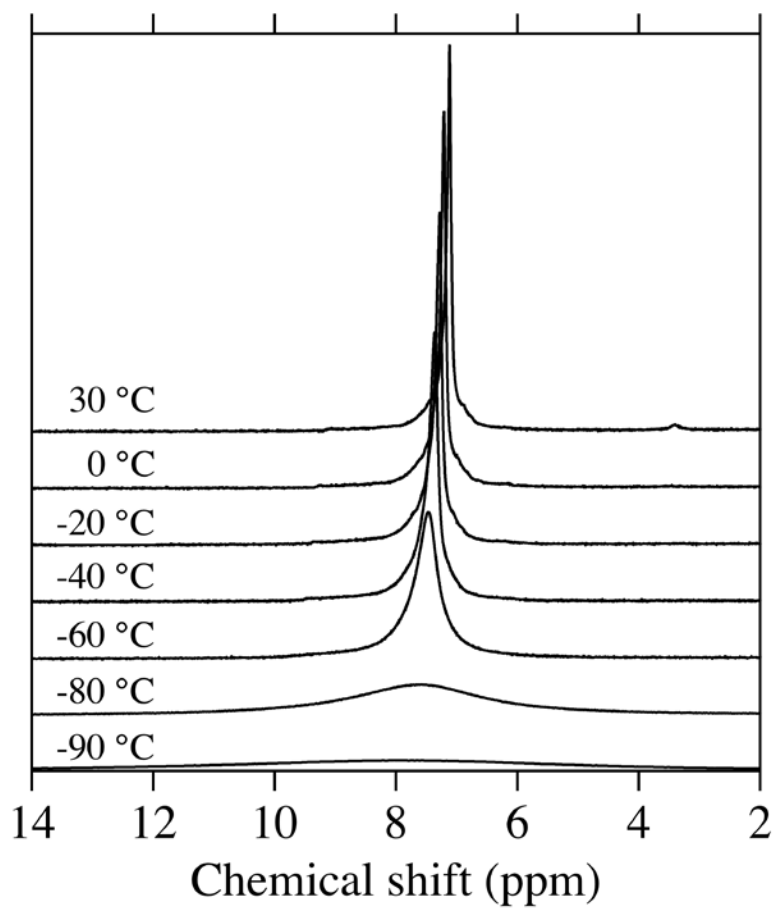


Figure 1. C. Wakai et al.

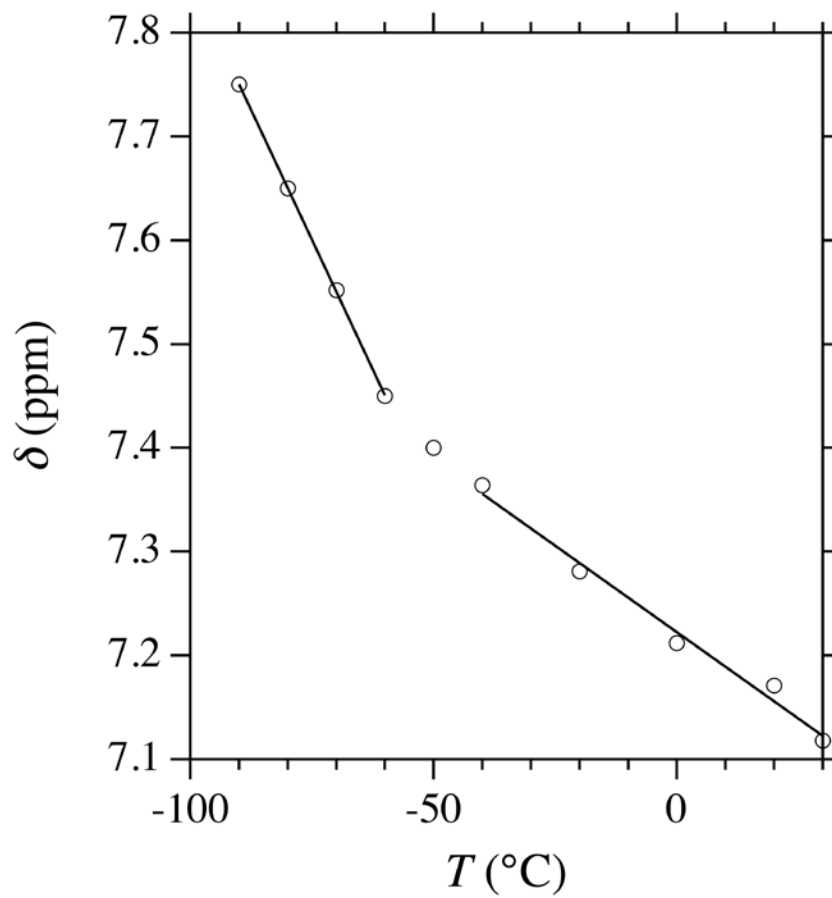


Figure 2. C. Wakai et al.

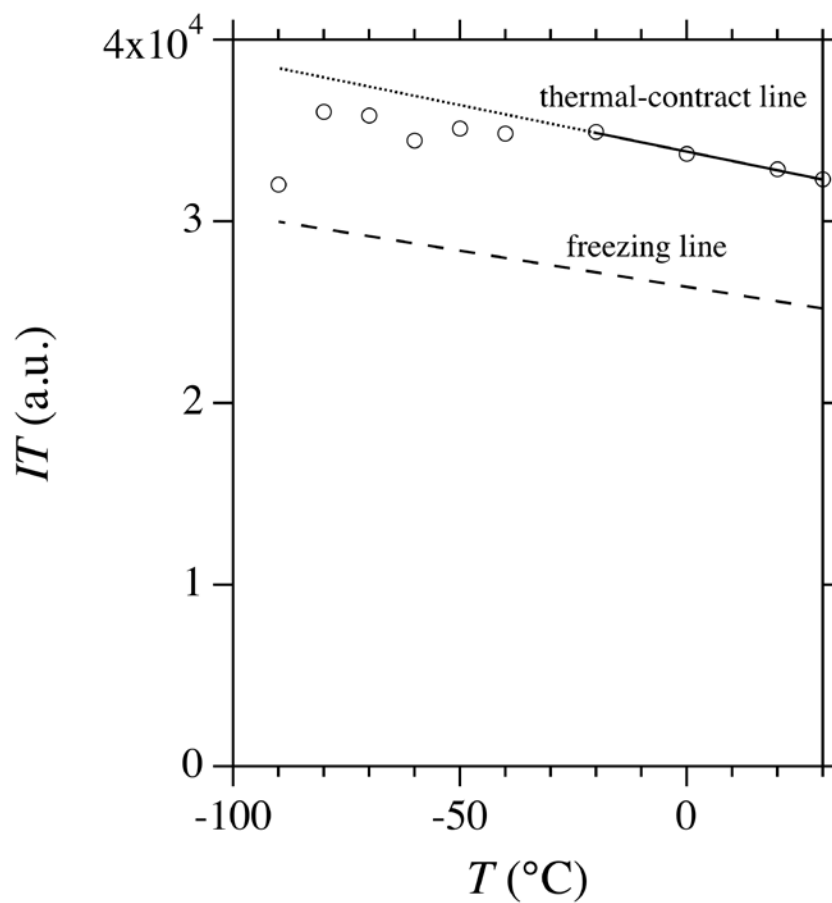


Figure 3. C. Wakai et al.

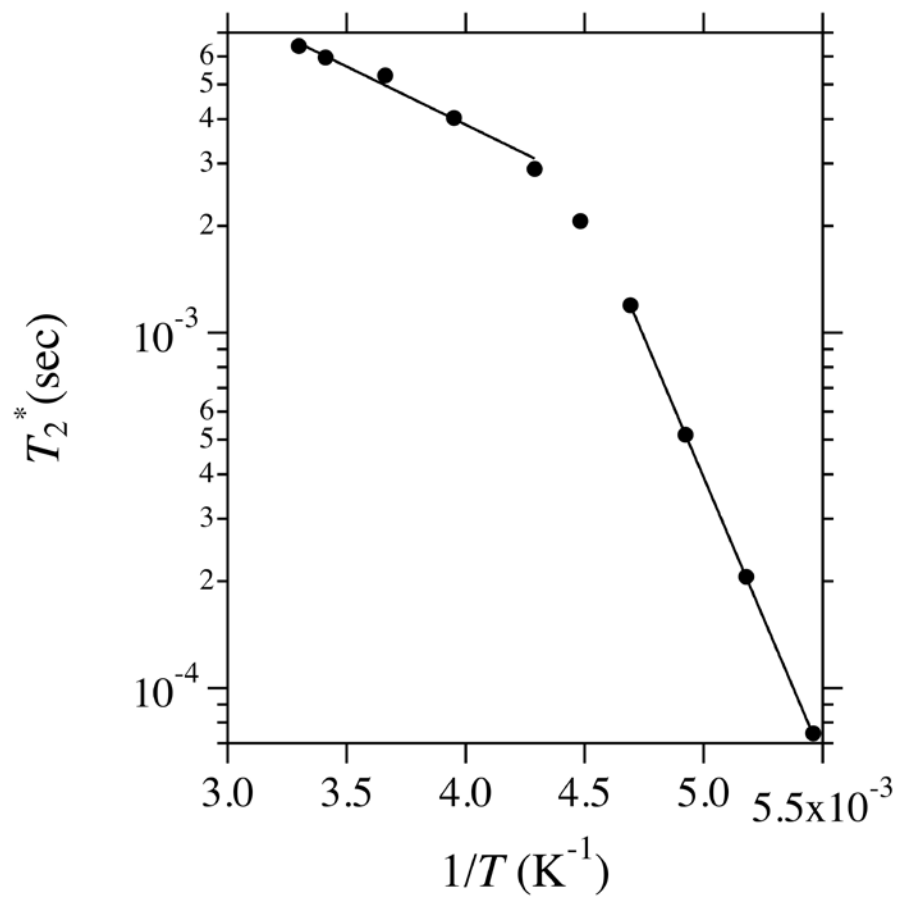


Figure 4. C. Wakai et al.

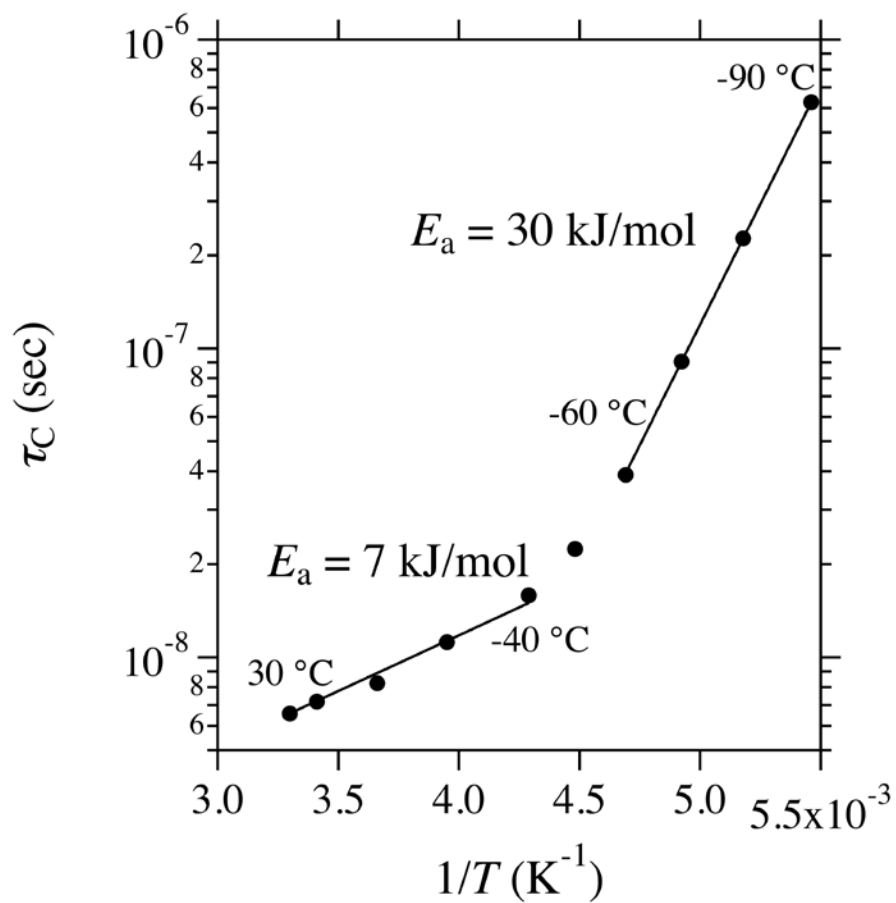


Figure 5. C. Wakai et al.



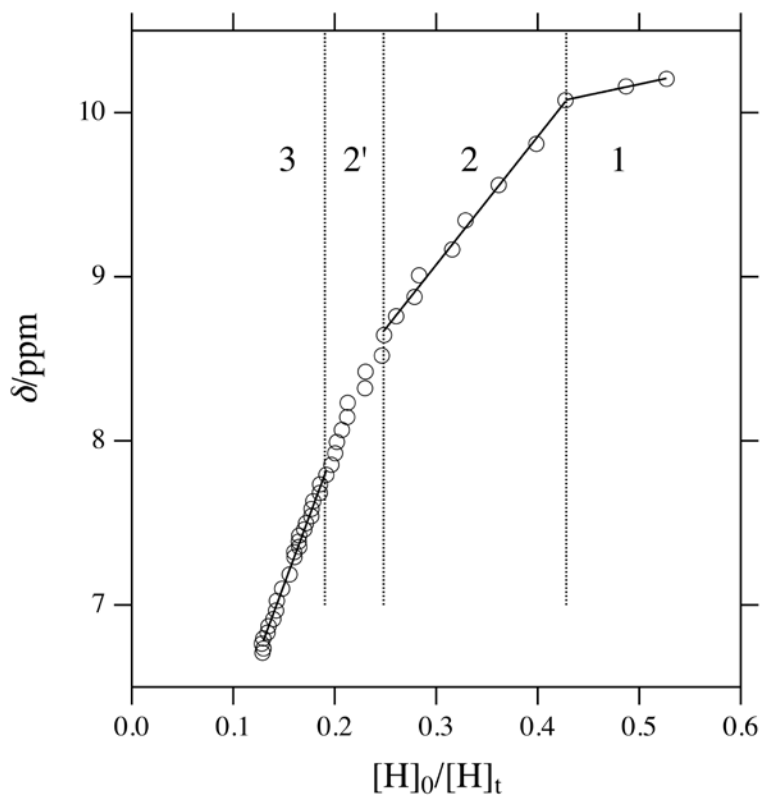


Figure S1. The  $^1\text{H}$  chemical shift ( $\delta$ ) vs. the reciprocal concentration of  $^1\text{H}$  normalized by the initial ( $[H]_0/[H]_t$ ).

C. Wakai et al.